

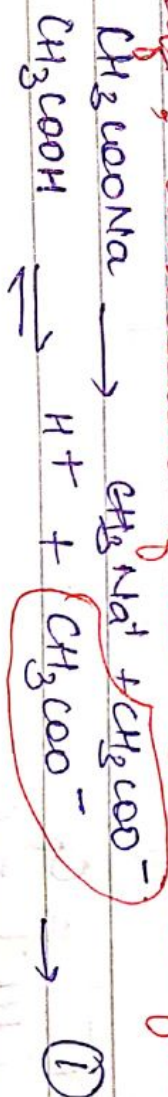


$\longrightarrow$ Electronegativity $\uparrow$ es.
 $\longrightarrow$ Acid strength $\uparrow$ es.

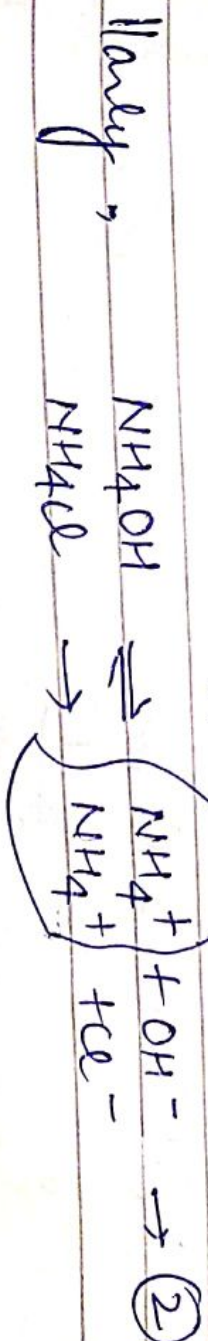
Common Ion effect in the Ionisation of Acids and Bases.

The shift in the eqbm on adding a substance that provides more of an ionic species already present in the dissociation eqbm. It is in accordance with Le Chatelier's principle.

So, If a salt of weak Acid is added to a solution of the acid itself, dissociation of the acid does further.



the addition of CH_3COO^- ions supplied by CH_3COONa pushes the eqbm to left (eqn (1)) as a result the dissociation of acetic acid is suppressed.



Mixture of weak Acids and salts:-

Suppose a weak monoprotic acid HA



$$K_a = \frac{[H^+][A^-]}{[HA]}$$

$$[H^+] = K_a \frac{[HA]}{[A^-]} \quad \text{--- (1)}$$

Now if there is a mixture of weak Acid and its strong salt NaA. let $C_1 = [HA]$ and $C_2 = [NaA]$

but know HA is weak Acid, so K_a is also very small which is further suppressed by common ion of NaA, $\therefore$ in the mixture $\Rightarrow$

$$[A^-] = C_2$$

$$\text{where as } [HA] = C_1.$$

so the equation (1) becomes

$$[H^+] = \frac{K_a C_1}{C_2}$$

$$\text{or in general } [H^+] = K_a \frac{C_1}{C_2}$$

$$= K_a \frac{[\text{Acid}]}{[\text{Salt}]}$$

So, as the ratio of acid/salt dec., the $[H^+]$ dec.

Ques what will be the hydrogen ion conc. of a solⁿ obtained by mixing 500 ml of 0.20M. Acetic Acid and 500 ml of 0.30M Sodium acetate? ($K_a(\text{AcH}) = 1.75 \times 10^{-5}$)

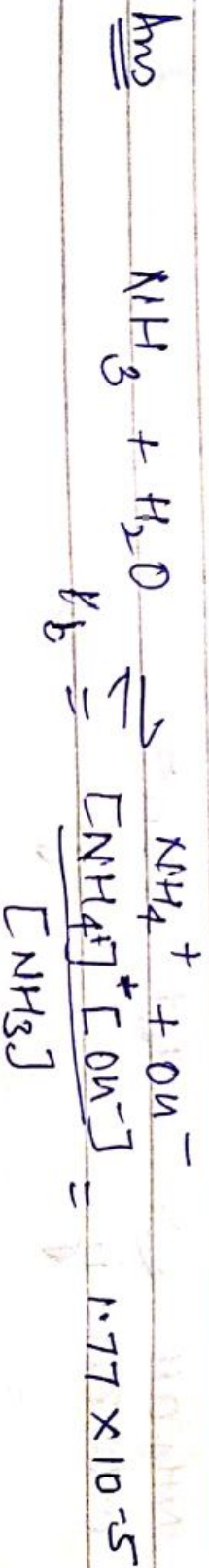
Soln $\therefore [AcH]$ in mixture = $\frac{0.20}{1000} \times 500 \text{ ml} = 0.10 \text{ M}$.

$[NaA] = \frac{0.30}{1000} \times 500 \text{ ml} = 0.15 \text{ M}$.

$$[H^+] = K_a \frac{[\text{Salt}]}{[\text{acid}]}$$

$$= \frac{1.75 \times 10^{-5} \times 0.15}{0.10} = 1.17 \times 10^{-5} \text{ mol/dm}^3.$$

Ques - Calculate the pH of a 0.10M of ammonia solution. Calculate the pH after 50.0 ml of this solution is treated with 25.0 ml of 0.10 M HCl. The dissociation constant of NH_3 $K_b = 1.77 \times 10^{-5}$.



So $[NH_4^+] = [OH^-] = x$ (Before Neutralization)

$$[NH_3] = 0.10 - x \approx 0.10$$

$$\therefore 1.77 \times 10^{-5} = \frac{(x)(x)}{0.10}$$

$$\Rightarrow x = 1.33 \times 10^{-3} = [OH^-]$$

$$\text{So } [H^+] = \frac{K_w}{[OH^-]} = \frac{10^{-14}}{1.33 \times 10^{-3}} = 7.51 \times 10^{-12}$$

$$pH = -\log(7.51 \times 10^{-12}) = 11.12.$$

On addn of 25 ml of 0.1M HCl soln.

$\therefore$ mmole of HCl = $0.1 \times 25 \text{ ml} \Rightarrow 2.5 \text{ mmol of HCl}$.

In 50.0 ml of 0.1M HCl $\Rightarrow 50 \times 0.10 \text{ M} = 5.0 \text{ mmole of } NH_3 \text{ soln}$.

After neutralization mmole of NH_3 left = 2.5 mmole.

Total volume of soln = $50 \text{ ml} + 25 \text{ ml} = 75 \text{ ml}$.

$\therefore$ the resulting soln conc = $2.5 \text{ mmole} \Rightarrow 0.0333 \text{ M}$
 $\frac{2.5 \text{ mmol}}{75 \text{ ml}}$



The final solⁿ already has 8.5 mmol NH_4^+ i.e. 0.033M
 $\therefore$ total conc of $[\text{NH}_4^+]^+ = 0.033 + y$
as y is small, $\therefore [\text{NH}_4\text{OH}] \approx 0.033\text{M}$ and $[\text{NH}_4^+] = 0.033\text{M}$

$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_4\text{OH}]} = \frac{y (0.033)}{(0.033)} = 1.77 \times 10^{-5}$$

$$[\text{OH}^-] = 1.77 \times 10^{-5} \text{ M}$$

$$[\text{H}^+] = \frac{K_w}{[\text{OH}^-]} = \frac{10^{-14}}{1.77 \times 10^{-5} \text{ M}} = 0.56 \times 10^{-9}$$

$$\boxed{\text{pH} = 9.24}$$

Buffer Solutions:-

The solutions which resist change in pH on dilution or with the addition of small amounts of acid or alkali are called buffer solutions.

many body fluids needs definite pH, it is also required in chemical and biochemical processes.

Many medical and cosmetic formulations require that are to be kept and administered at a particular pH.

Buffer capacity:- The capacity of a solution to resist alteration in its pH.

Buffer Index :- (β)

$$\beta = \frac{dB}{d(pH)}$$

dB = amount of strong base added to buffer.

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So it is the amount of alkali required to change the pH of a buffer solution by unity.

The quantity dB is given in moles per 100 g of the solvent.

β is always a positive quantity.

Addⁿ of a strong acid is equivalent to negative addⁿ of base, that is dB becomes $-dB$ and $d(pH)$ becomes $-d(pH)$ as pH lies on the addⁿ of the acid) $\therefore \beta$ is +ve.

Buffer solⁿs are considered to possess reserve acidity as well as reserve alkalinity. $\therefore$ NH_4Ac has reserve acidity due to presence of NH_4^+ ions and reserve alkalinity due to presence of CH_3COO^- ions.

MOST OF THE IMPORTANT BUFFER SOLUTIONS USUALLY CONSIST OF MIXTURE OF EITHER WEAK ACIDS AND THEIR SALTS OR WEAK BASES AND THEIR SALTS.

I) Buffer Mixture of a weak acid and its salt:-

a common buffer:- equimolar solⁿ of Acetic Acid and sodium acetate.

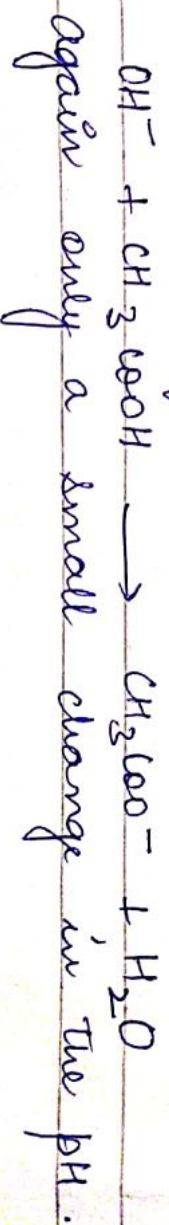
AcH weakly dissociated when as NaAc being a strong electrolyte, completely dissociated

So Now suppose a strong acid is added to above mix.
 H^+ will be taken up by CH_3COO^- to form slightly dissociated CH_3COOH .

$\therefore$ In a way the H^+ ions are neutralized by the acetate ions present in the mixture. There is a very little change in the pH of the mixture.



On the other hand if OH^- ions are added



II Buffer Mixture of a weak Base and its salt Equimolar of NH_4OH and NH_4Cl

This mixture has undissociated NH_4OH and NH_4^+ and Cl^- .

If a strong acid is added



If strong base is added,



so here reserve acidity is due to NH_4^+ and reserve alkalinity is due to NH_4OH .

~~alkalita~~